

## Development of intein-inspired amide cleavage chemical device

Chiaki Komiya<sup>†</sup>, Keisuke Aihara<sup>†</sup>, Ko Morishita, Hao Ding, Tsubasa Inokuma, Akira Shigenaga, Akira Otaka<sup>\*</sup>

<sup>†</sup>*Contributed equally*

*Institute of Biomedical Sciences and Graduate School of Pharmaceutical Sciences, Tokushima University,  
Shomachi, Tokushima 770-8505, Japan*

E-mail:

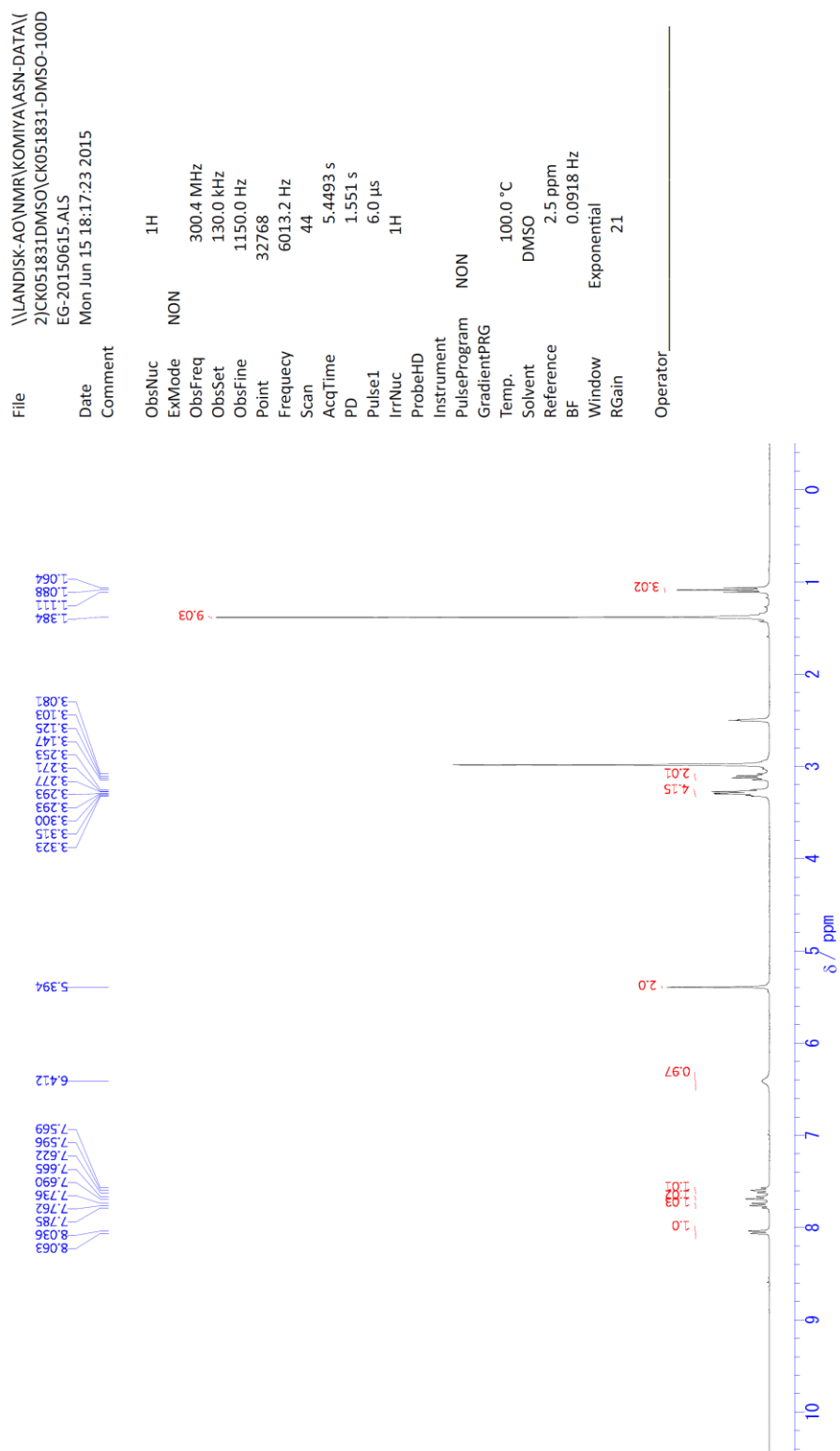
aotaka@ph.tokushima-u.ac.jp

## SUPPORTING INFORMATION

### Content:

Copies of NMR spectra for all compounds ..... p. S2

# 2-Nitrobenzyl {2-[(*tert*-butoxycarbonyl)amino]ethyl}ethylcarbamate **3**

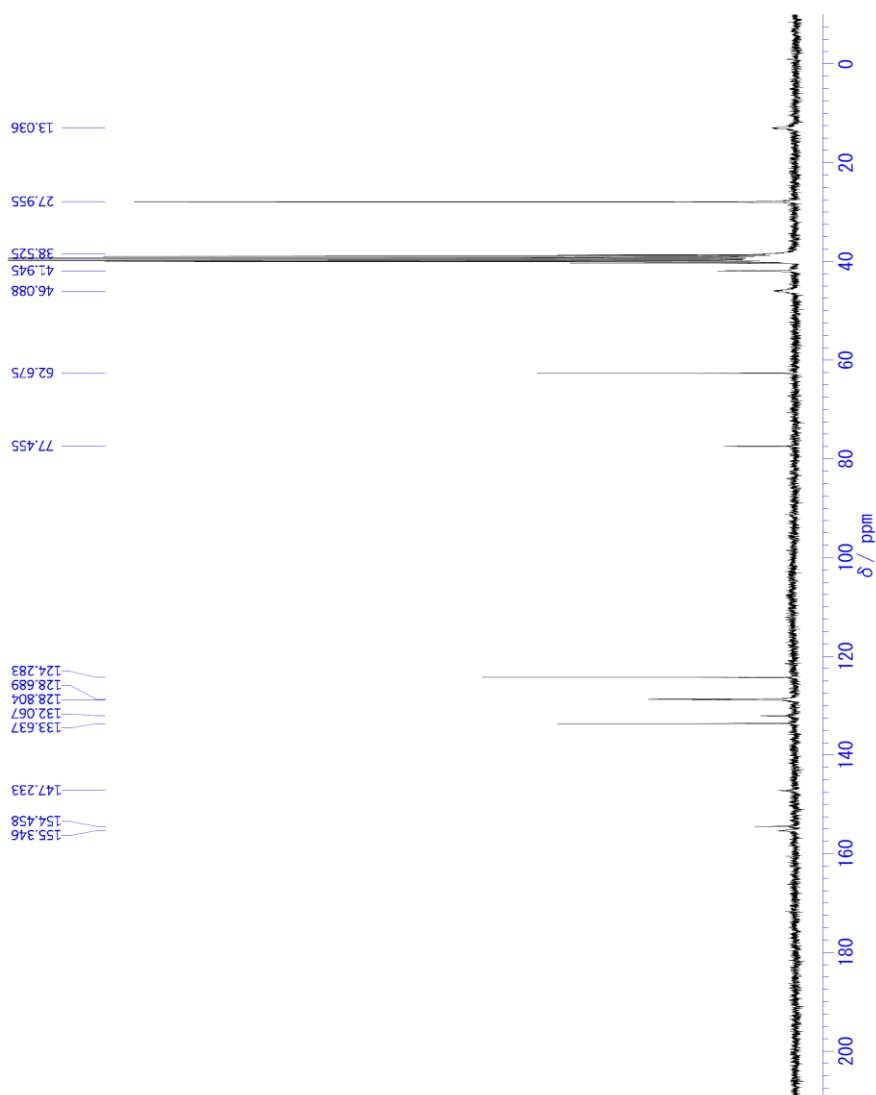


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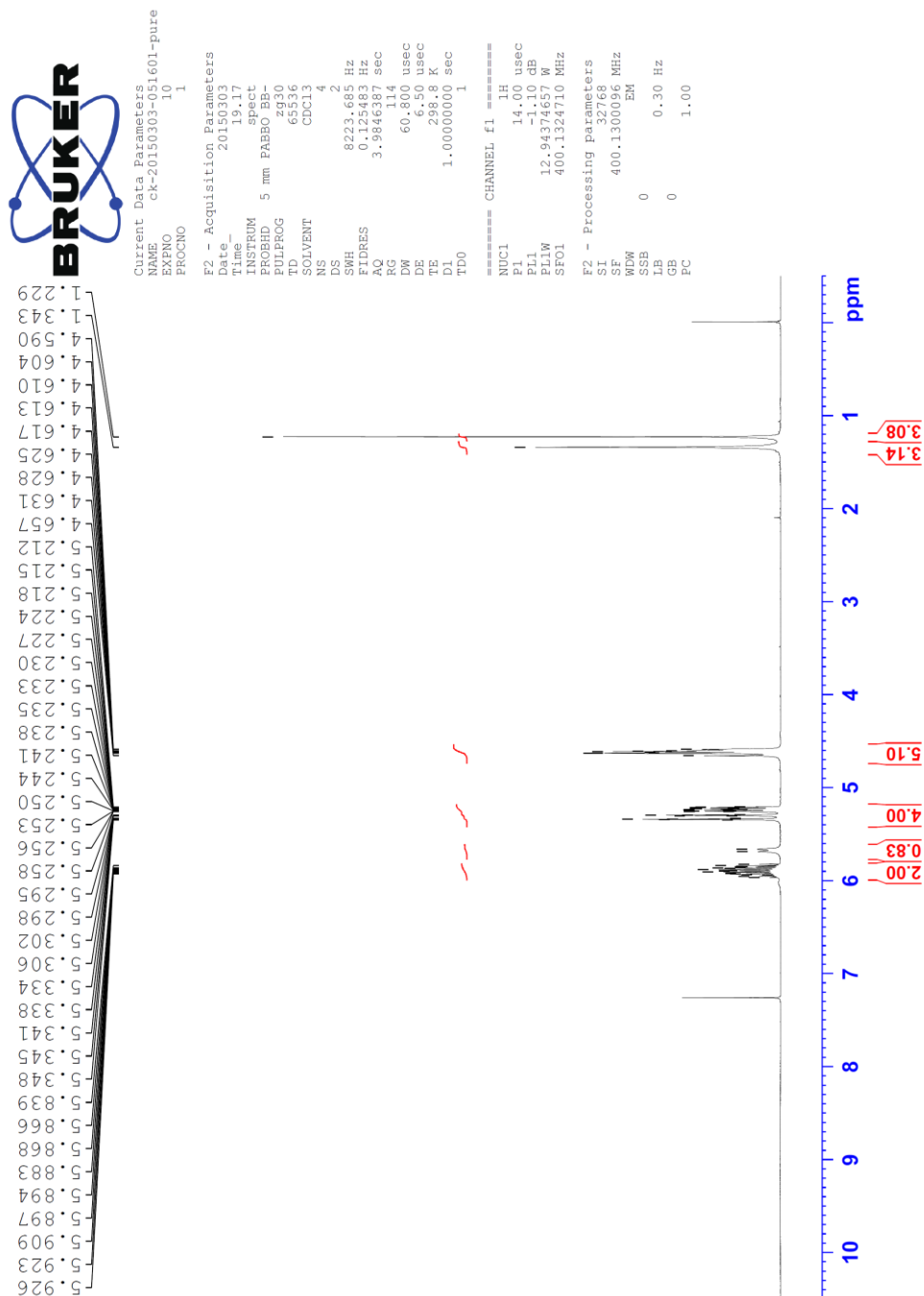
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Instrument  
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Reference 39.52 ppm  
BF 0.3106 Hz  
Window Exponential  
RGain 26

Operator

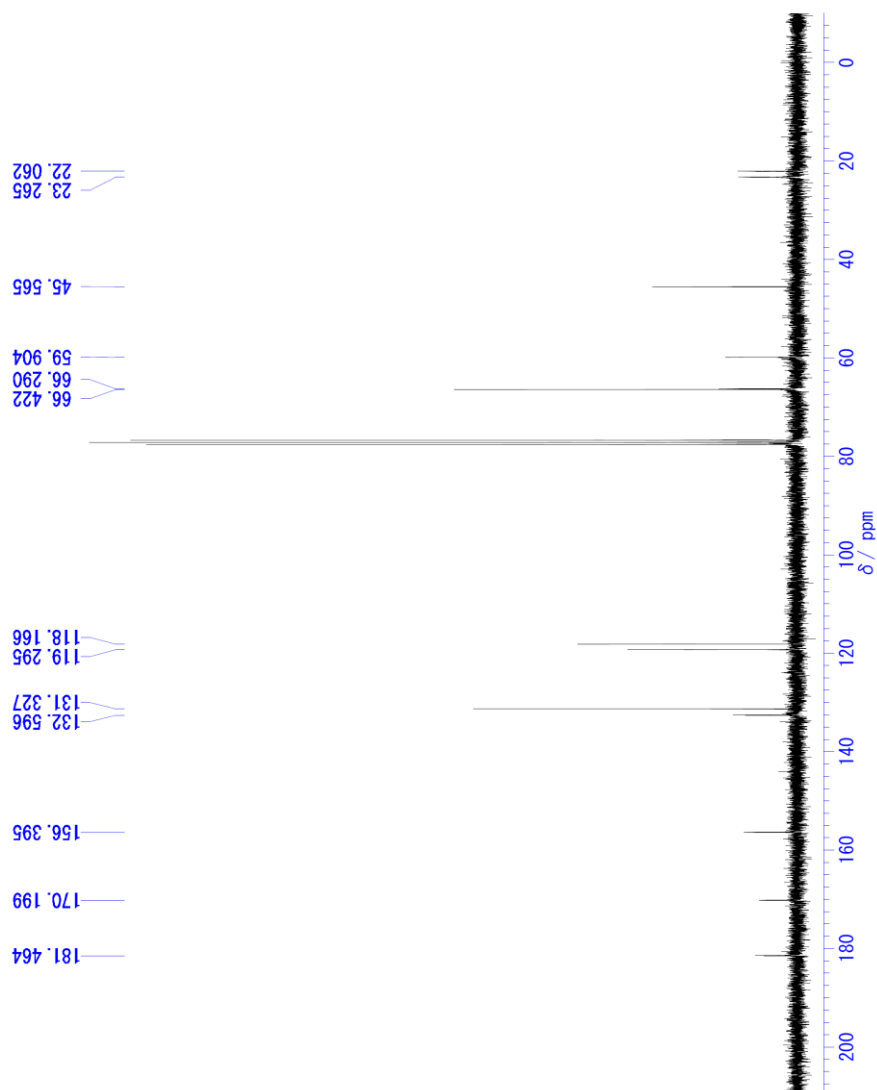


(S)-3-[[[(Allyloxy)carbonyl]amino]-2,2-dimethylsuccinic acid 4-(allyl)ester **8**

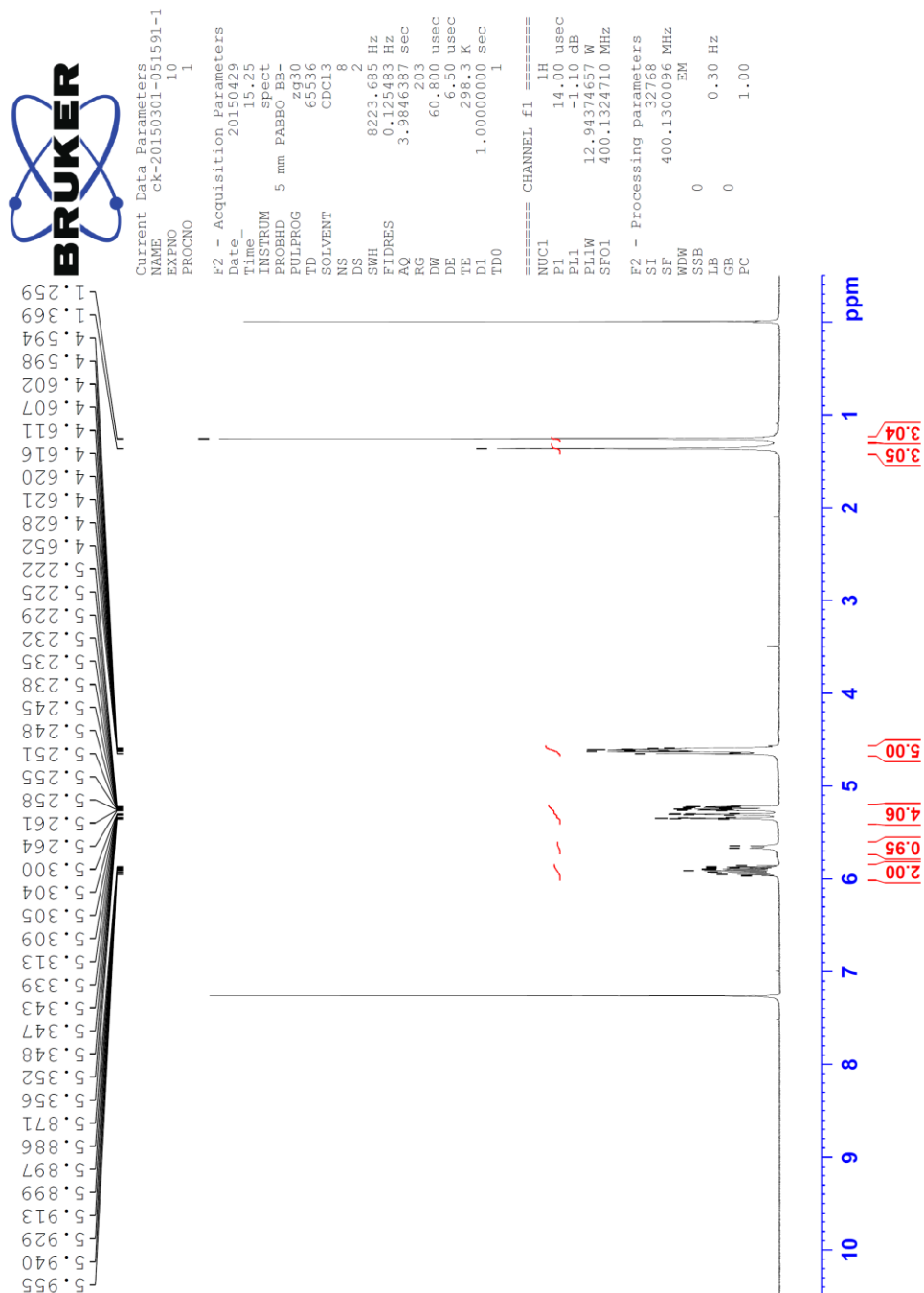


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Solvent	CDCL3
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RGain	24
Operator	



(S)-4-(allyloxy)-2-[[[(allyloxy)carbonyl]amino]-3,3-dimethyl-4-oxobutanoic acid **17**

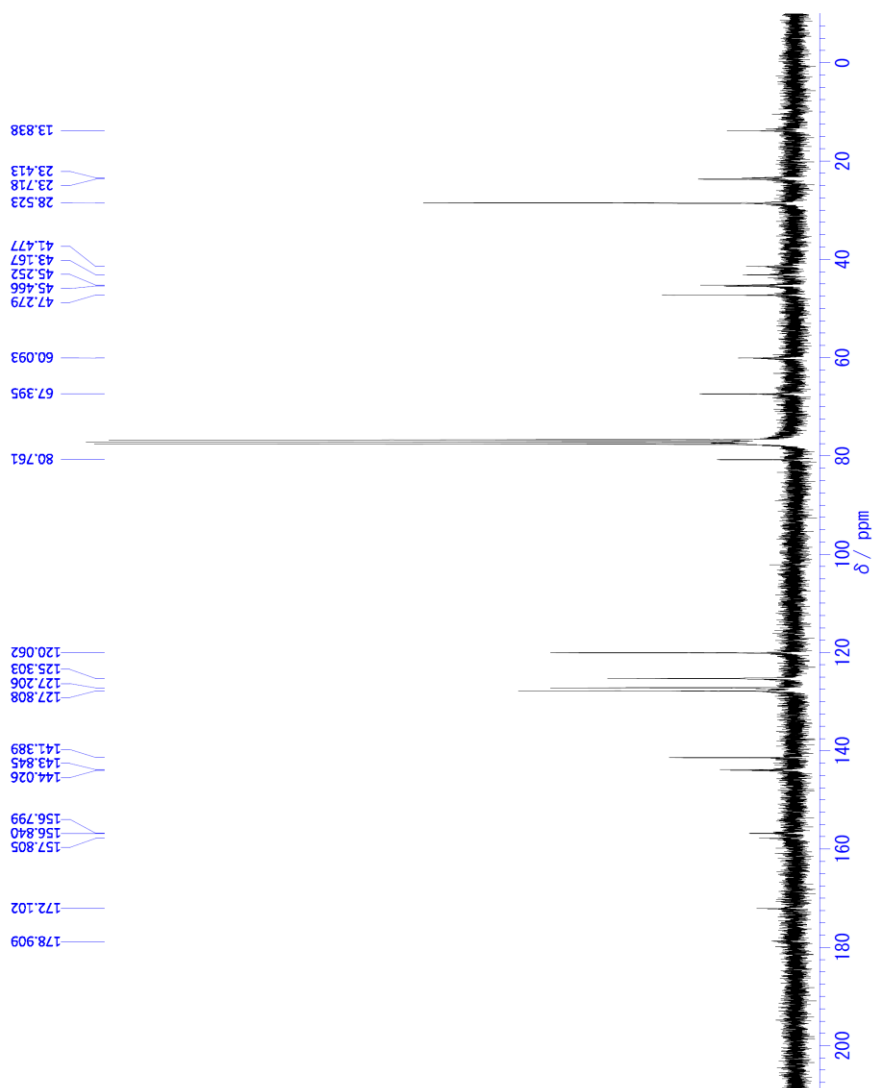


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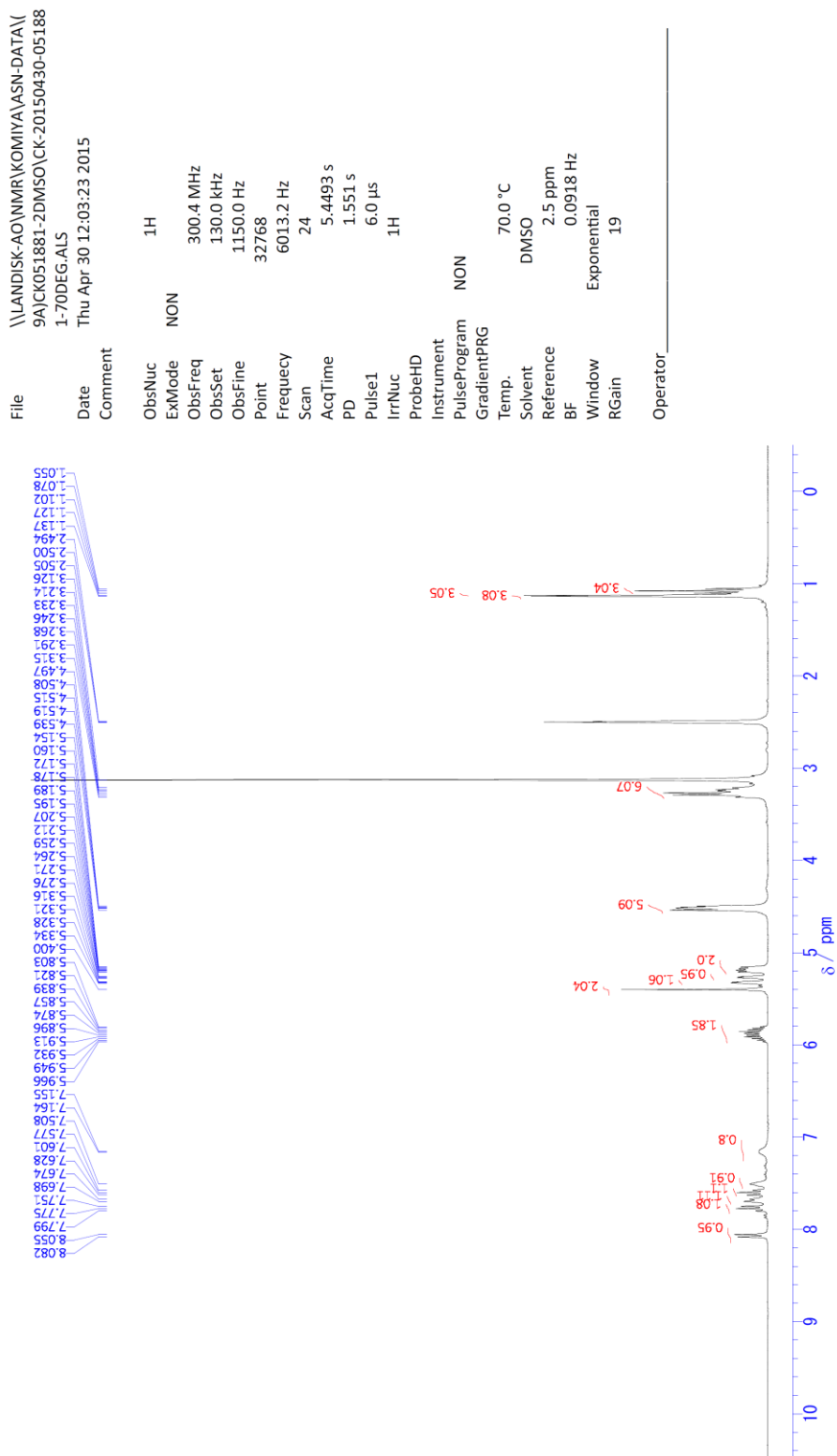
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BF 0.3114 Hz  
Window Exponential  
RGain 24

Operator



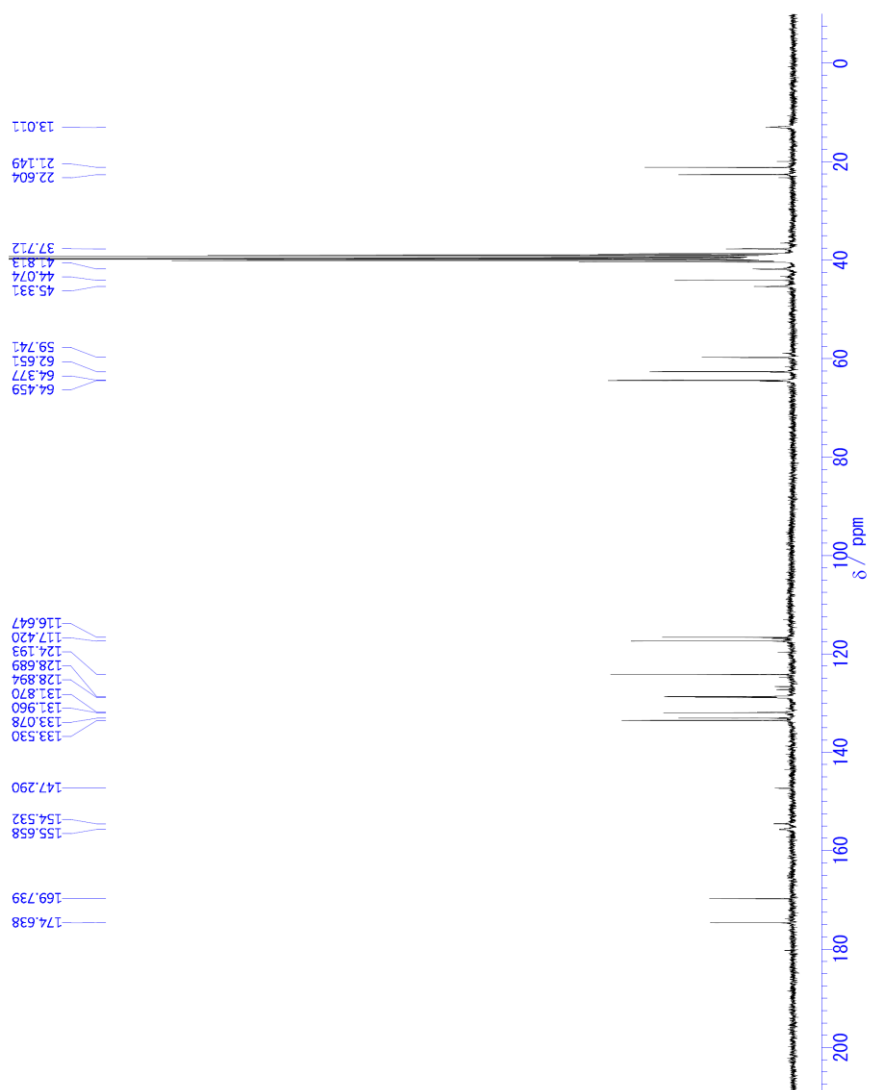
Allyl (S)-2-{[(allyloxy)carbonyl]amino}-4-{[2-ethyl(2-nitrobenzyloxycarbonyl)aminoethyl]amino}-  
3,3-dimethyl-4-oxobutanoate **9a**



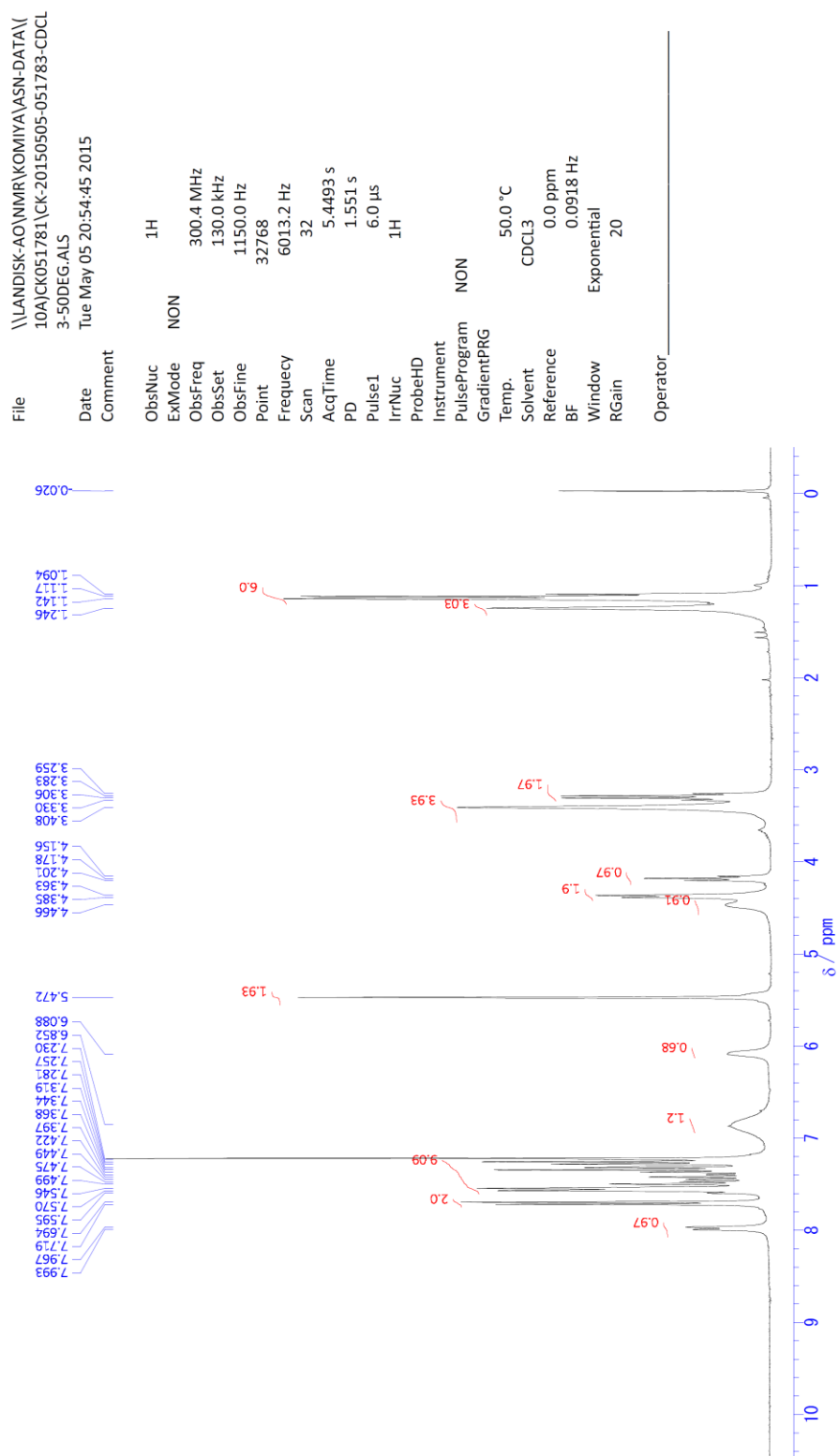


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Operator	

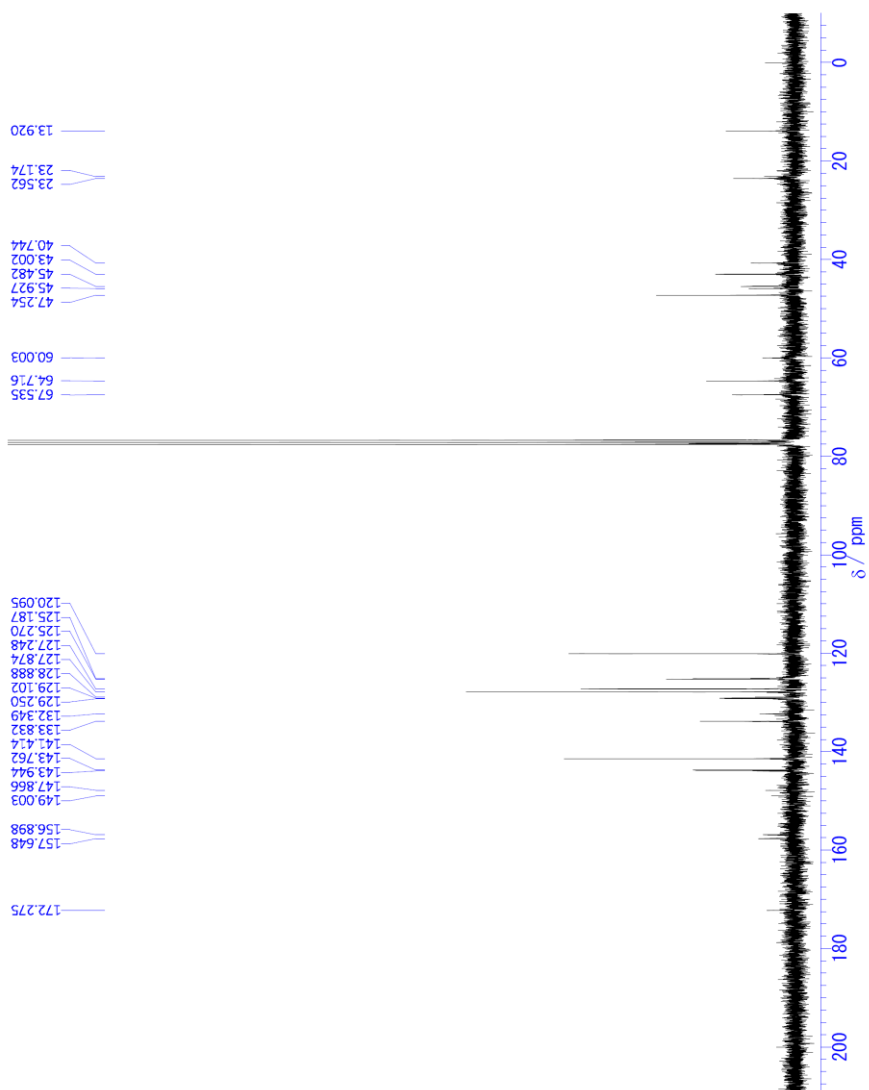


(*S*)-2-[[[(9H-Fluoren-9-yl)methoxycarbonyl]amino]-4-{[2-ethyl(2-nitrobenzyloxycarbonyl)amino ethyl]amino}-3,3-dimethyl-4-oxobutanoic acid **10a**

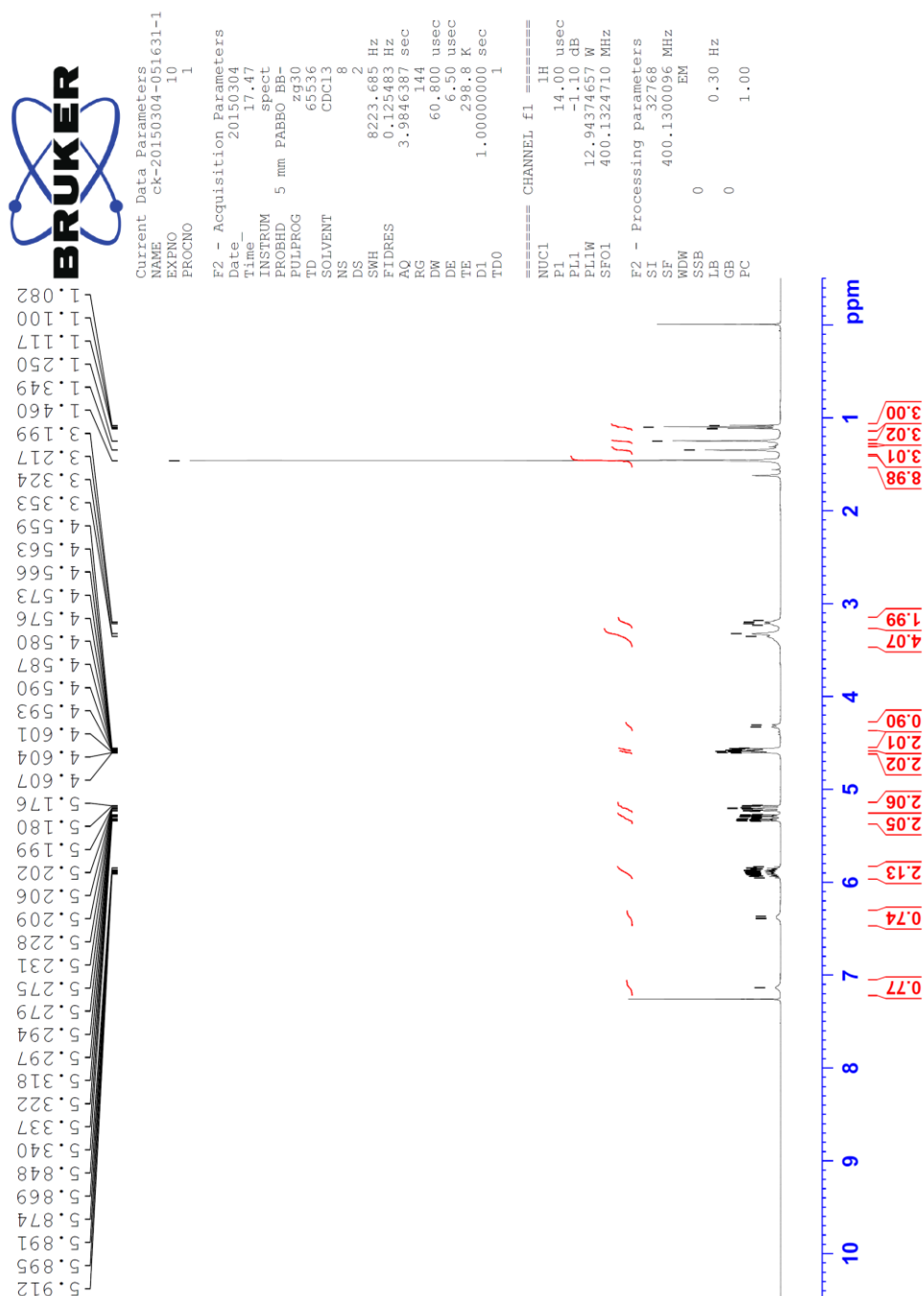


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IrrNuc	1H
ProbeHD	
Instrument	BCM
PulseProgram	
GradientPRG	
Temp.	25.0 $^{\circ}$ C
Solvent	CDCL3
Reference	77.16 ppm
BF	0.3114 Hz
Window	Exponential
RGain	24
Operator	



Allyl (S)-2-{[(allyloxy)carbonyl]amino}-4-{[2-(*tert*-butoxycarbonyl)(ethyl)aminoethyl]amino}-3,3-dimethyl-4-oxobutanoate **9b**

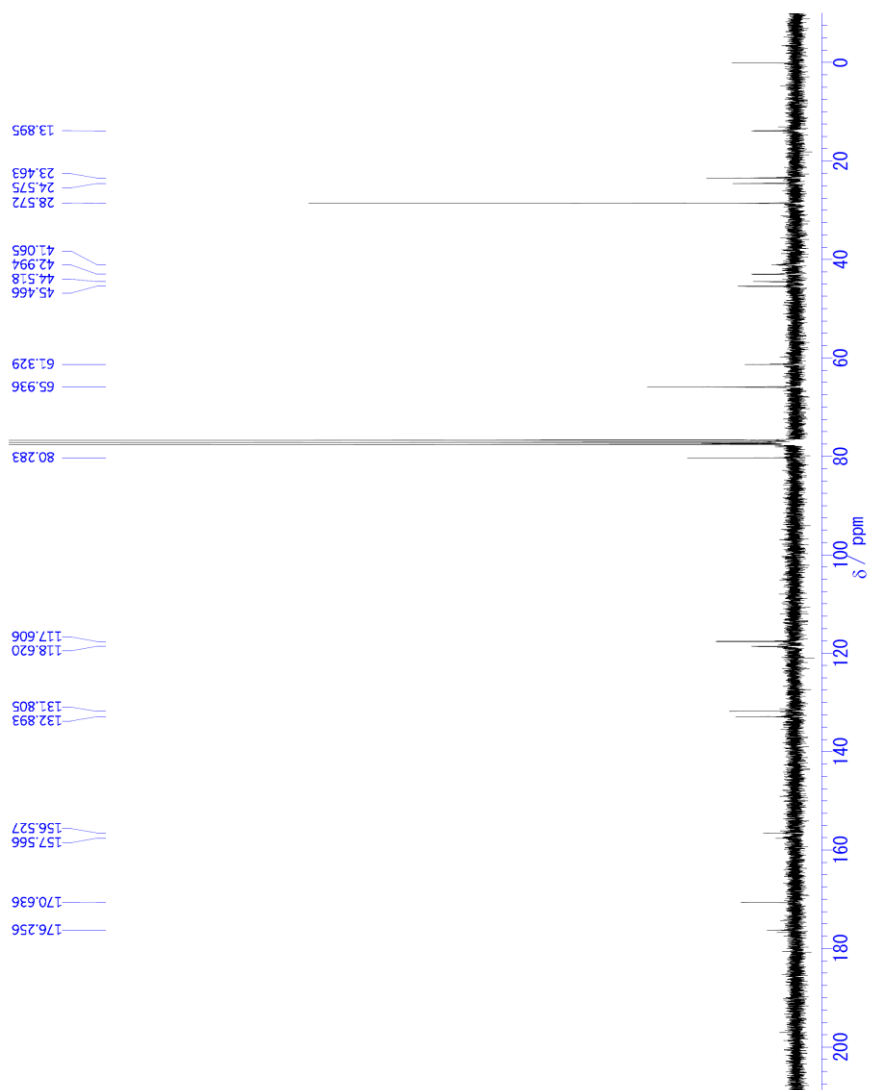


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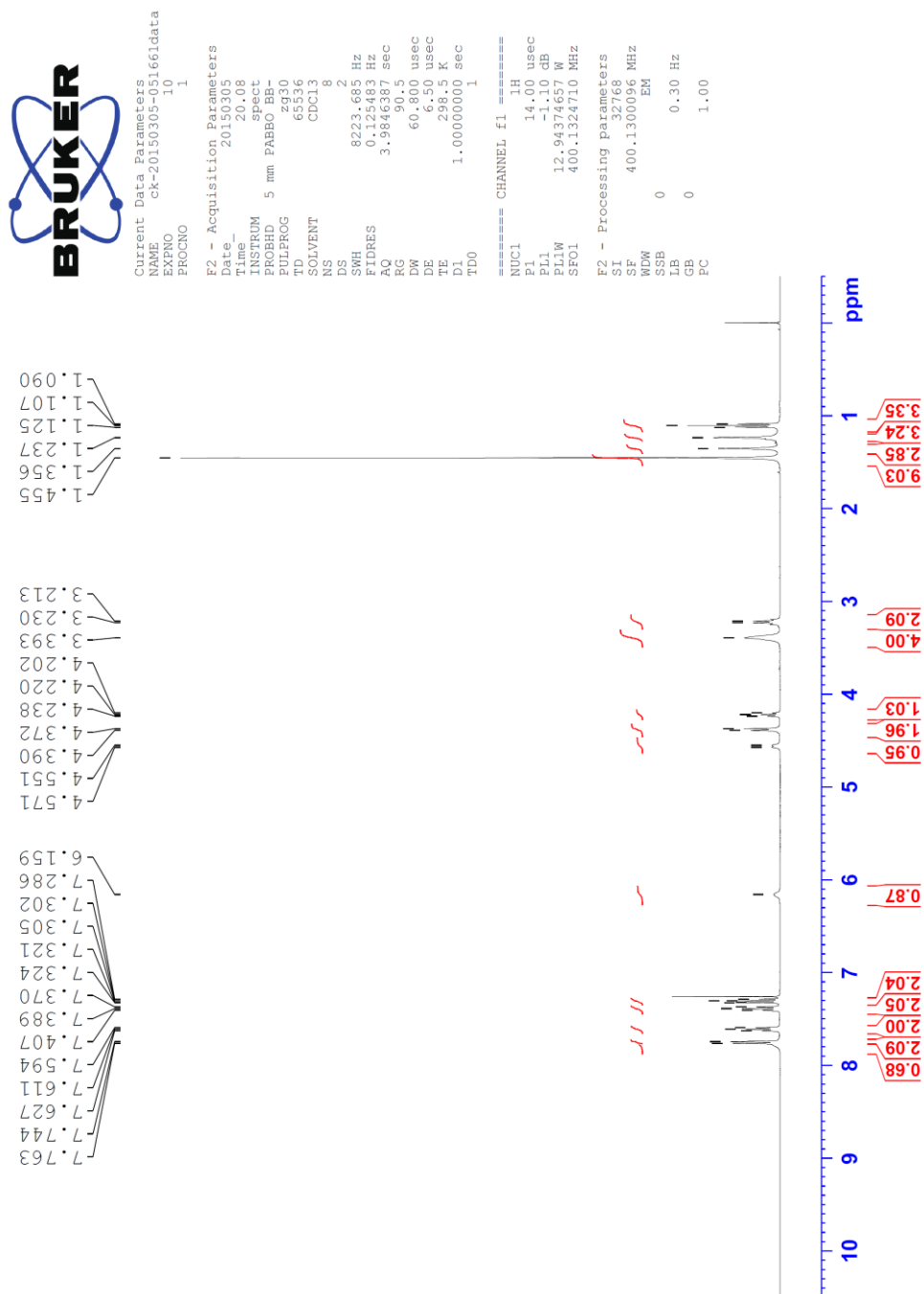
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Pulse1	5.0 $\mu$ s
IrrNuc	$^1\text{H}$
ProbeHD	
Instrument	
PulseProgram	BCM
GradientPRG	
Temp.	20.0 $^{\circ}\text{C}$
Solvent	CDCL <sub>3</sub>
Reference	77.16 ppm
BF	0.3114 Hz
Window	Exponential
RGain	24

Operator \_\_\_\_\_



(S)-2-{-[(9H-Fluoren-9-yl)methoxycarbonyl]amino}-4-{[2-(*tert*-butoxycarbonyl)(ethyl)aminoethyl]amino}-3,3-dimethyl-4-oxobutanoic acid **10b**

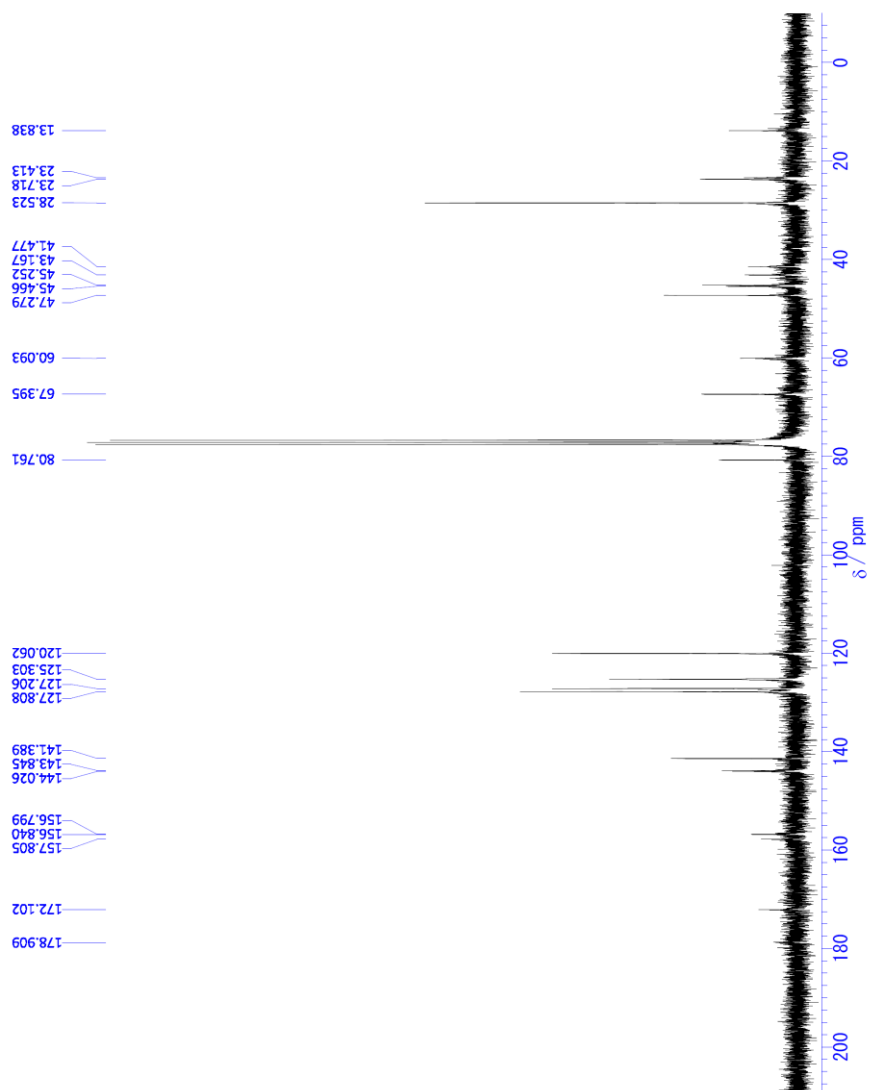


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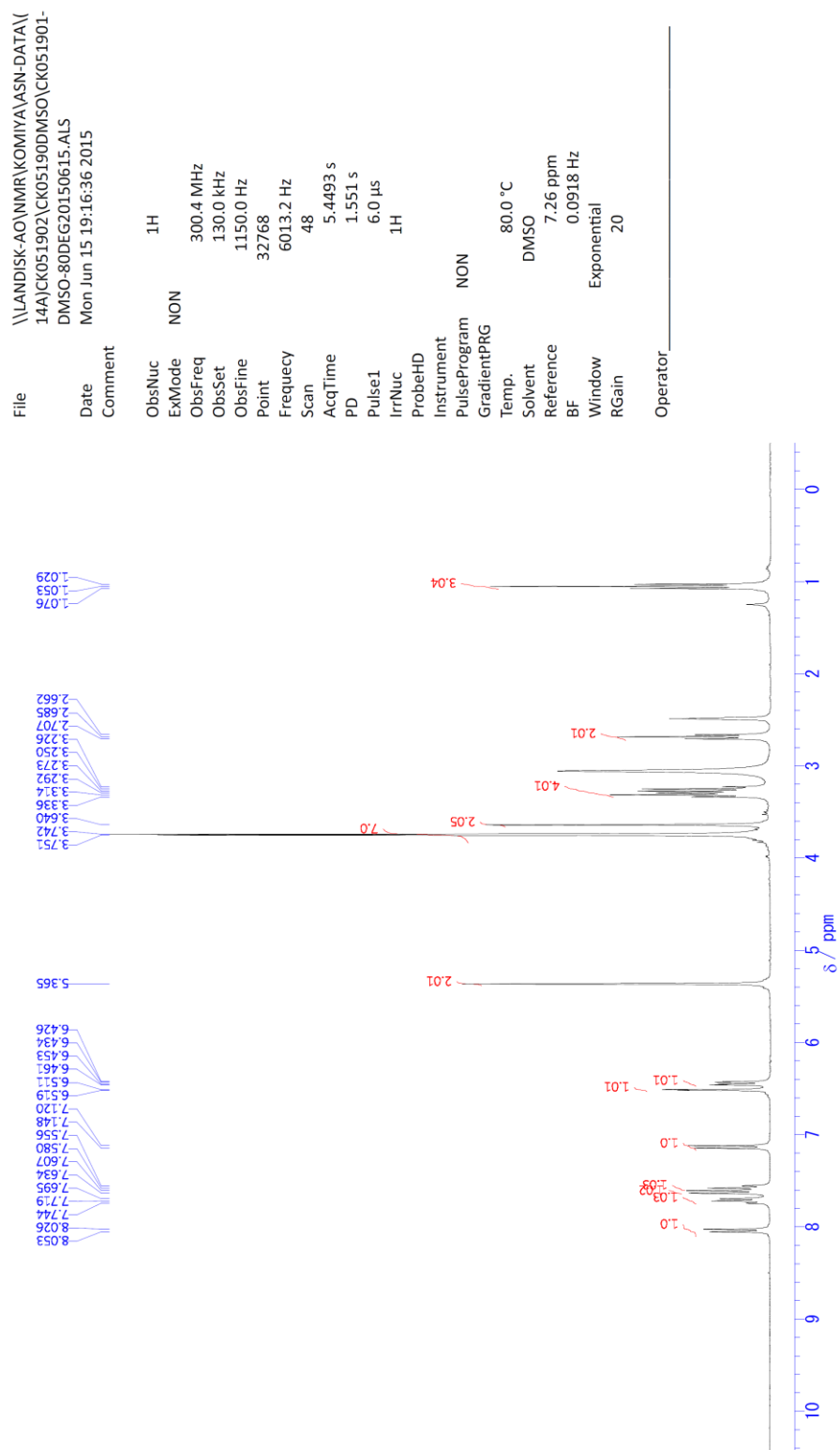
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Pulse1 5.0  $\mu$ s  
IrrNuc 1H  
ProbeHD  
Instrument  
PulseProgram BCM  
GradientPRG  
Temp. 25.0 °C  
Solvent CDCL3  
Reference 77.16 ppm  
BF 0.3114 Hz  
Window Exponential  
RGain 24

Operator



2-Nitrobenzyl {2-[(2,4-dimethoxybenzyl)amino]ethyl}(ethyl)carbamate **14a**



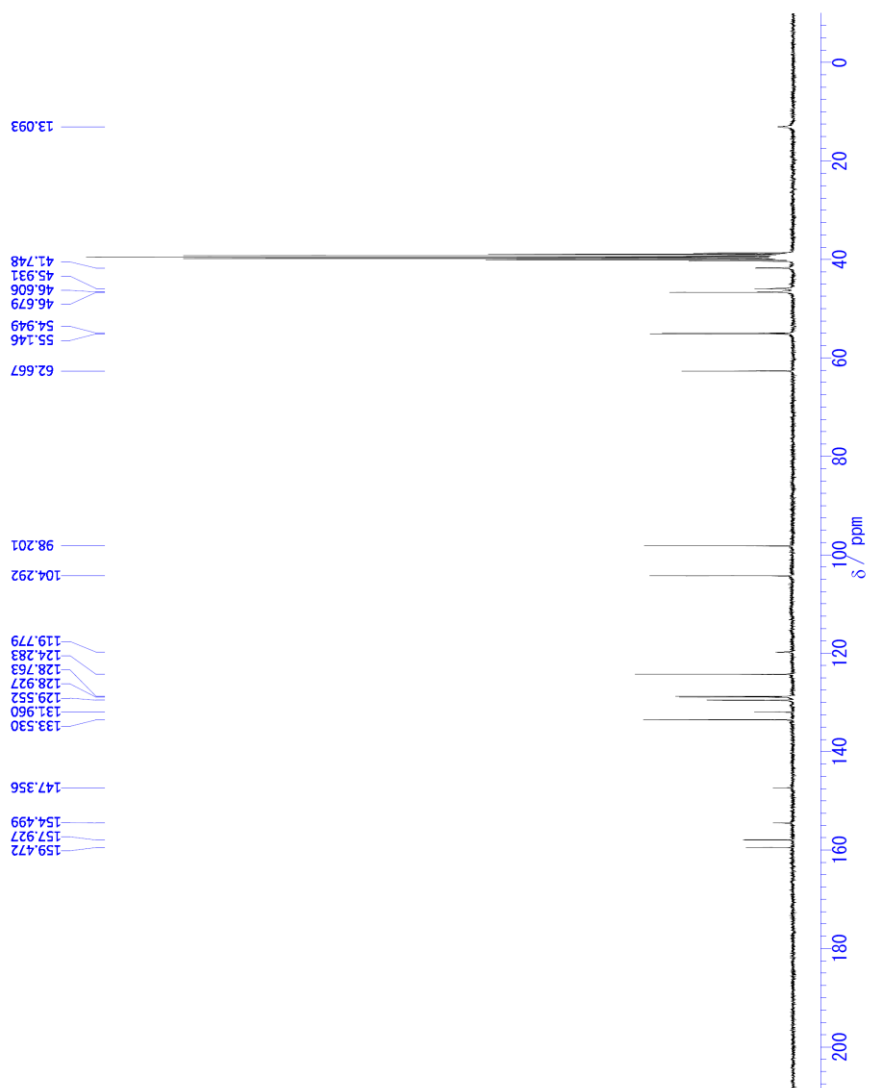


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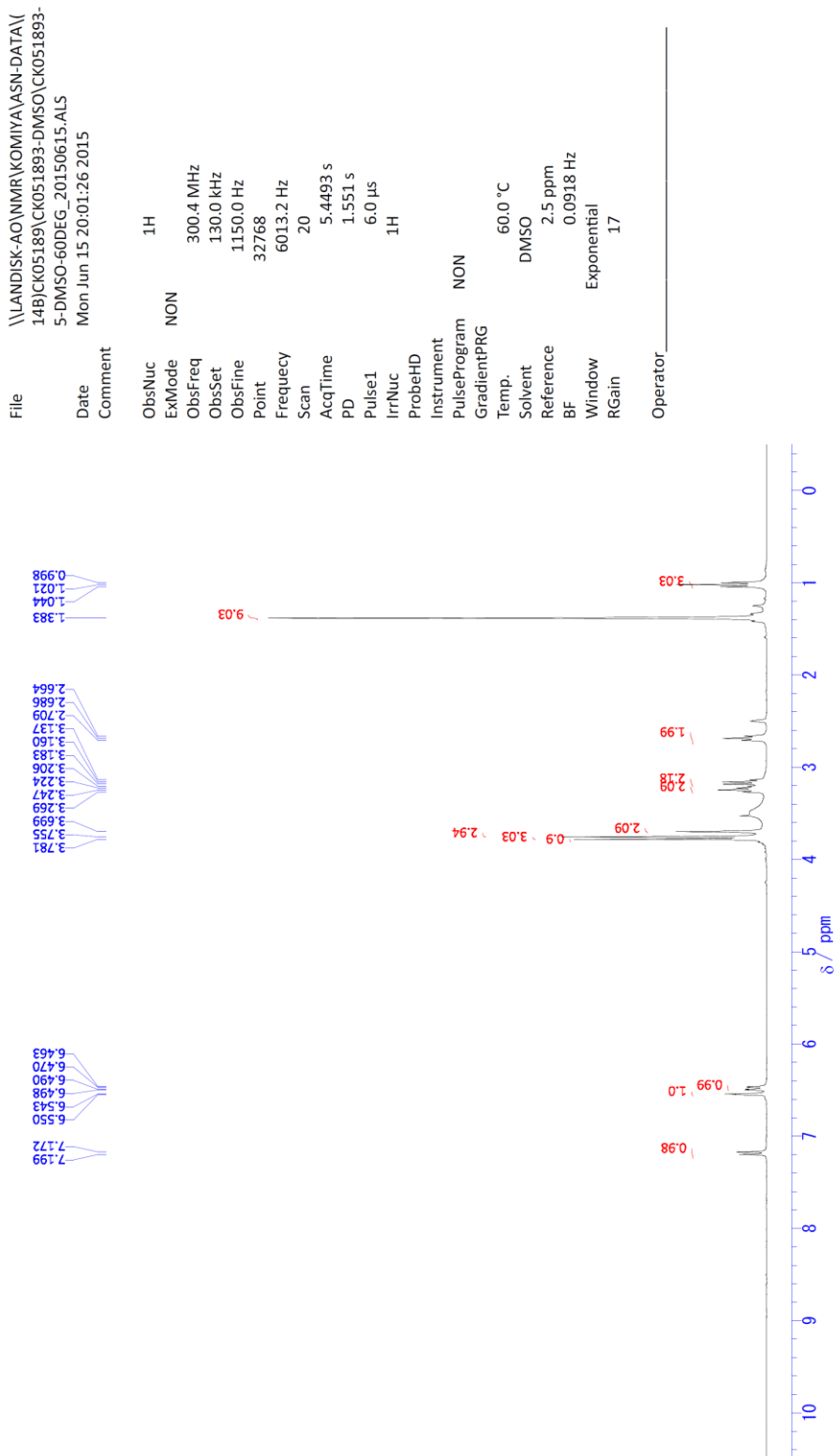
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Solvent DMSO  
Reference 39.52 ppm  
BF 0.3106 Hz  
Window Exponential  
RGain 26  
Operator



*tert*-Butyl {2-[(2,4-dimethoxybenzyl)amino]ethyl}(ethyl)carbamate **14b**

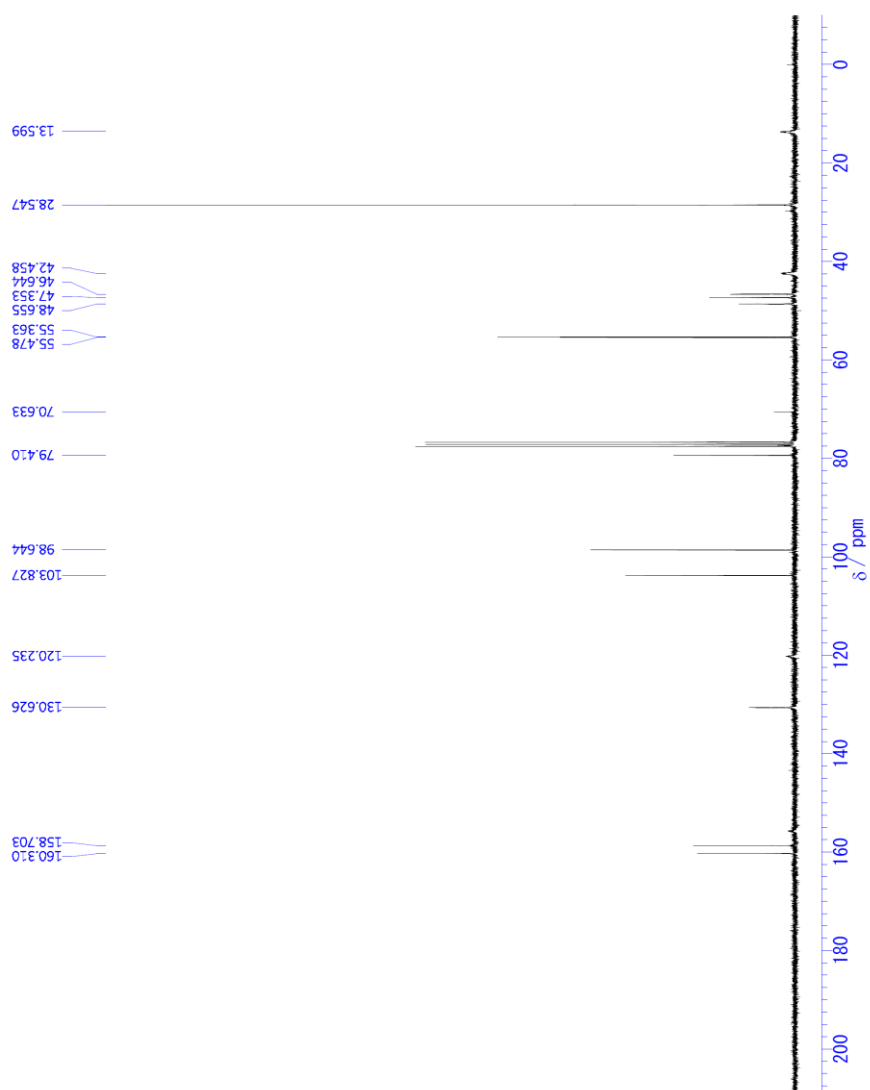


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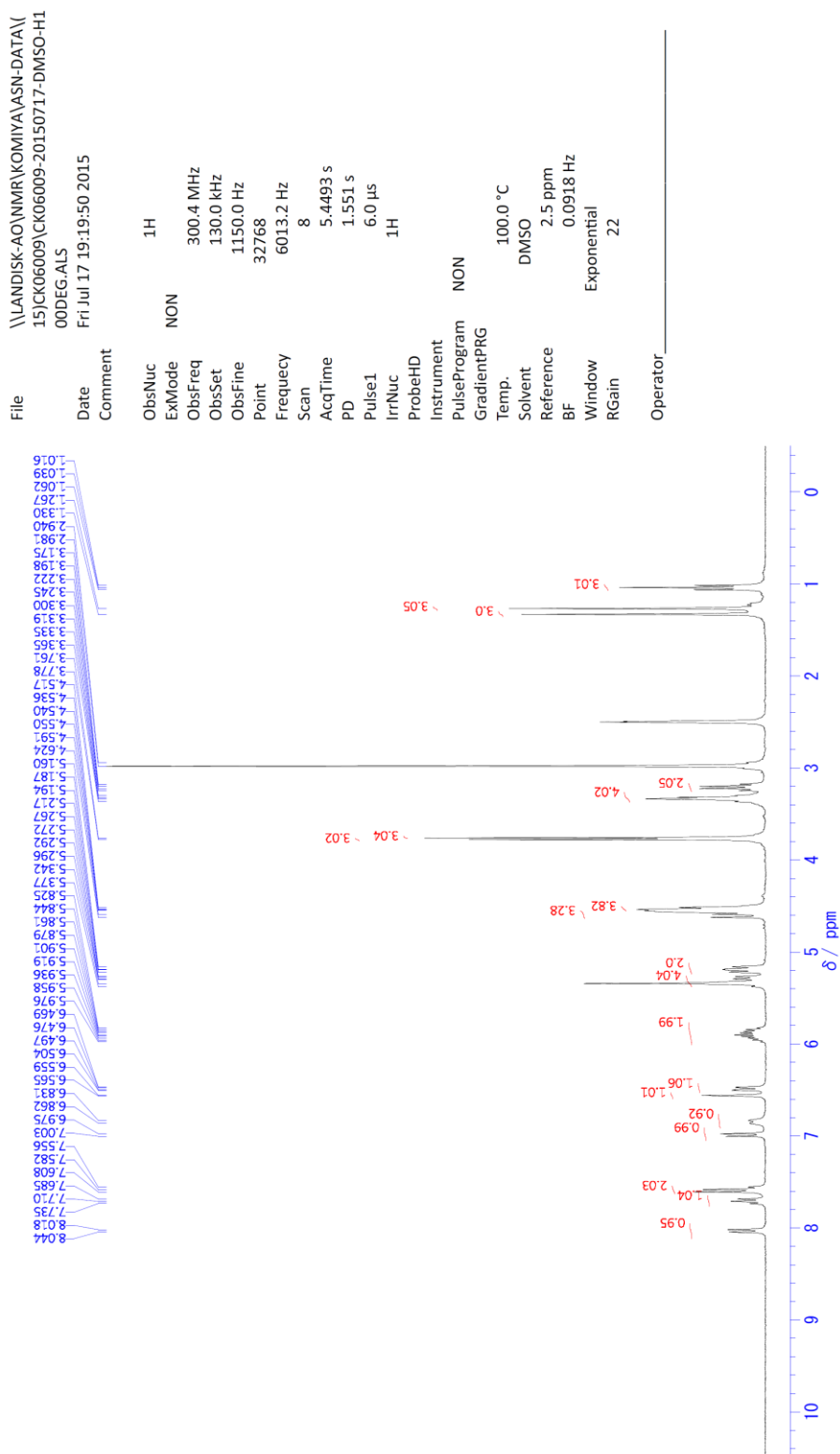
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ProbeHD	
Instrument	
PulseProgram	BCM
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Reference	77.16 ppm
BF	0.3114 Hz
Window	Exponential
RGain	24

Operator

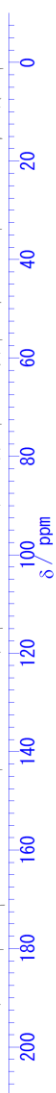


Allyl (S)-2-[(allyloxycarbonyl)amino]-4-[(2,4-dimethoxybenzyl)(2-ethyl-2-nitrobenzyloxycarbonyl aminoethyl)amino]-3,3-dimethyl-4-oxobutanoate **15**

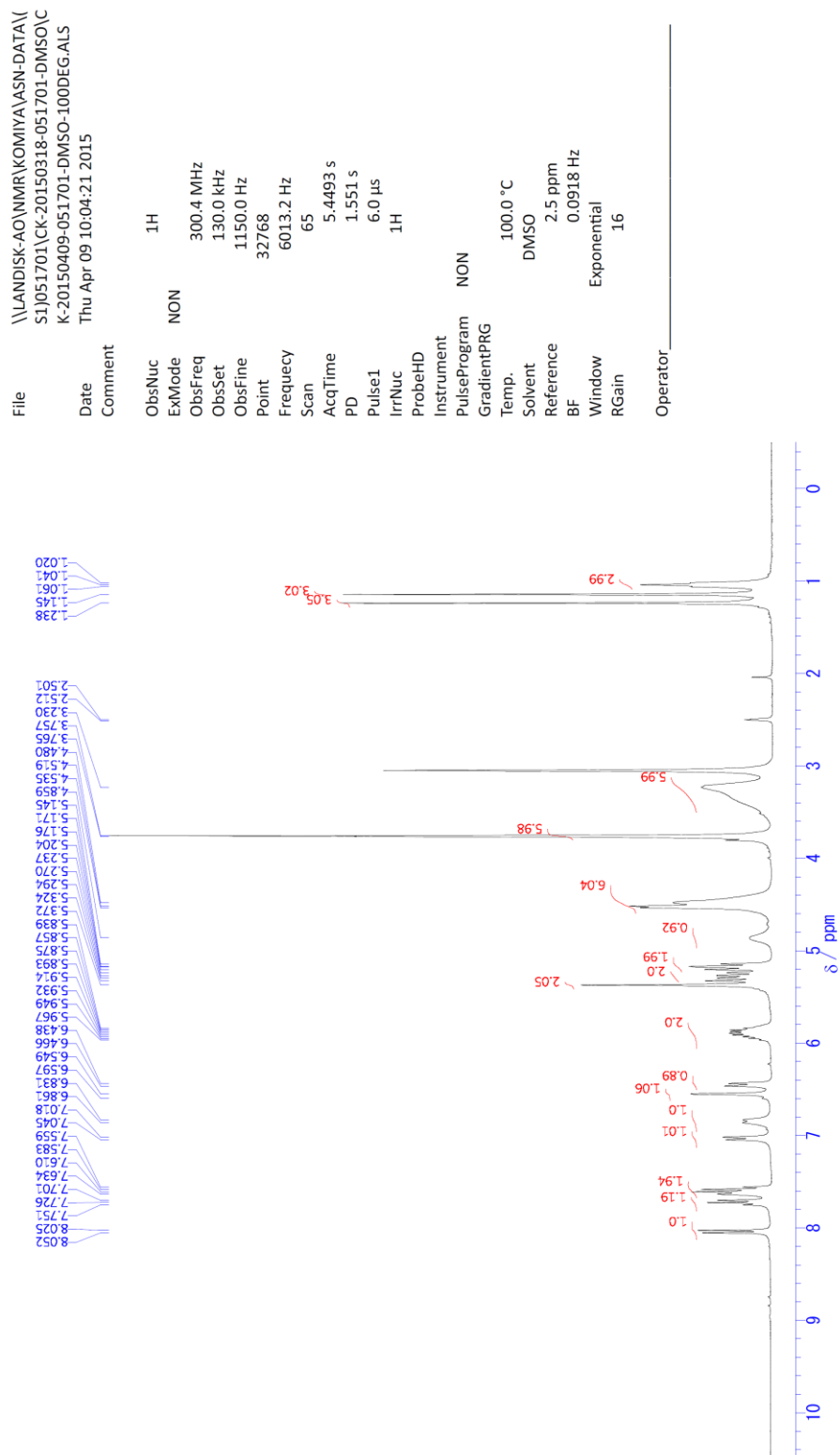


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Tue Jul 14 12:27:42 2015

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24.196	24.261																								
25.338	25.503																								
29.629	42.427																								
43.068	43.627																								
43.726	44.129																								
44.252	45.518																								
45.518	46.398																								
47.614	55.127																								
55.291	63.166																								
63.166	63.544																								
63.741	65.673																								
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116.998	117.368																								
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117.466	117.935																								
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118.099	124.774																								
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124.848	128.210																								
128.210	128.284																								
128.284	128.415																								
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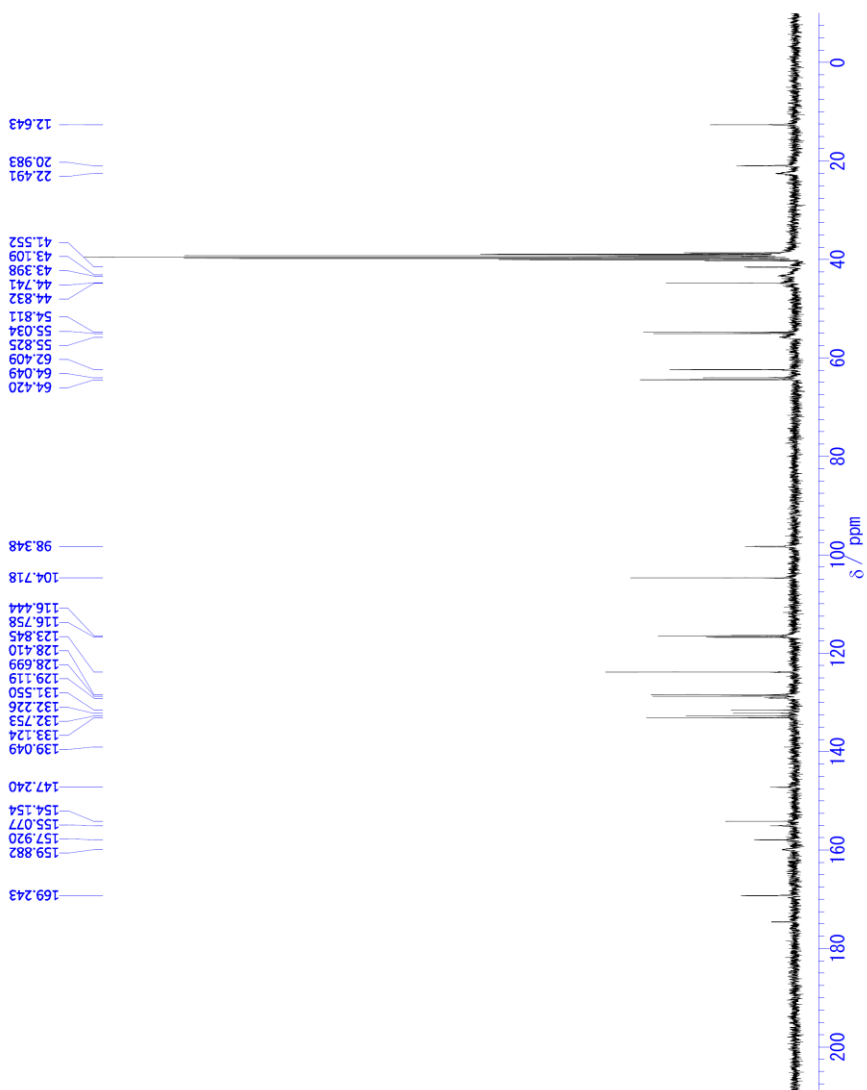


Allyl (S)-3-(allyloxycarbonyl)amino-4-[[2,4-dimethoxybenzyl][2-(ethyl-2-nitrobenzyloxycarbonyl amino)ethyl]amino}-2,2-dimethyl-4-oxobutanoate **25**

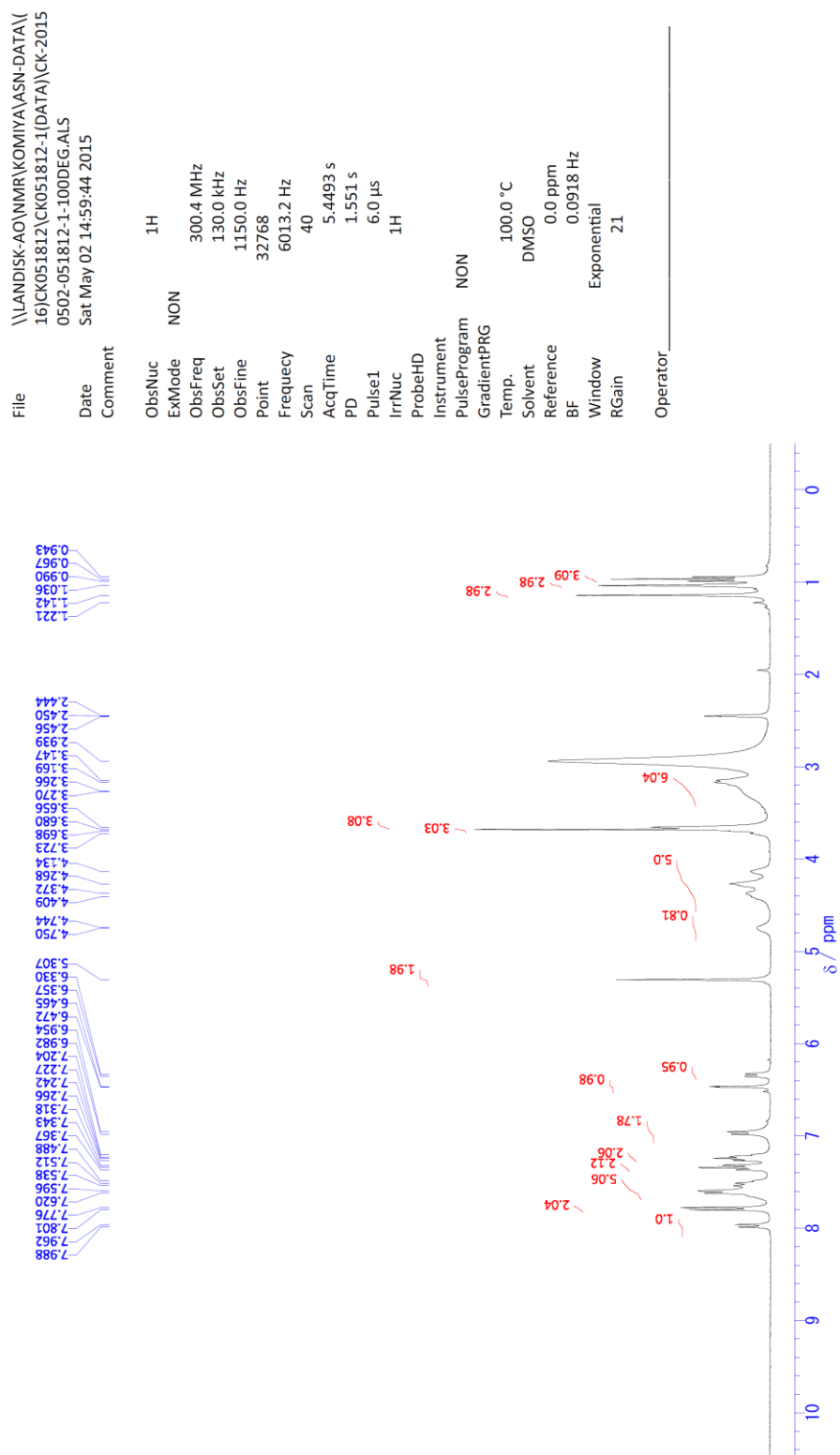


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 Instrument  
 PulseProgram BCM  
 GradientPRG  
 Temp. 100.0  $^{\circ}$ C  
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 BF 0.3114 Hz  
 Window Exponential  
 RGain 26  
 Operator



(*S*)-3-[[[(9H-Fluoren-9-yl)methoxycarbonyl]amino]-4-{[2,4-dimethoxybenzyl][2-ethyl(2-nitrobenzyl  
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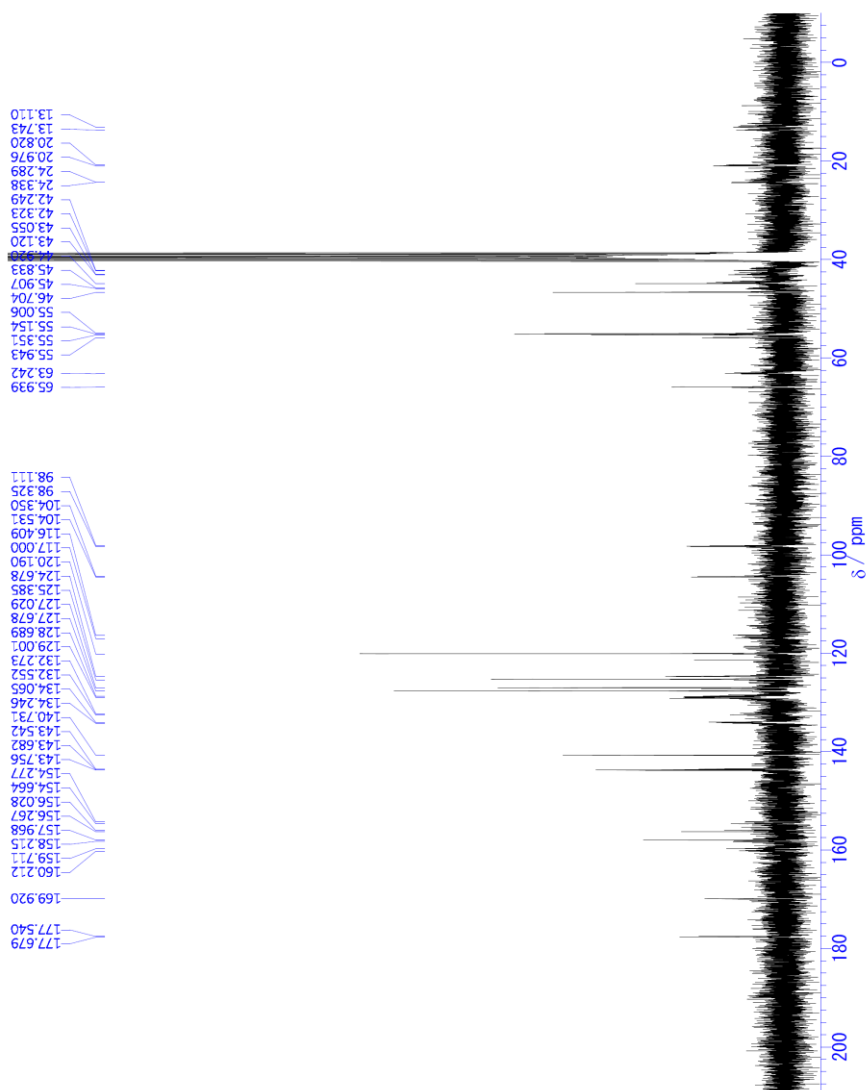


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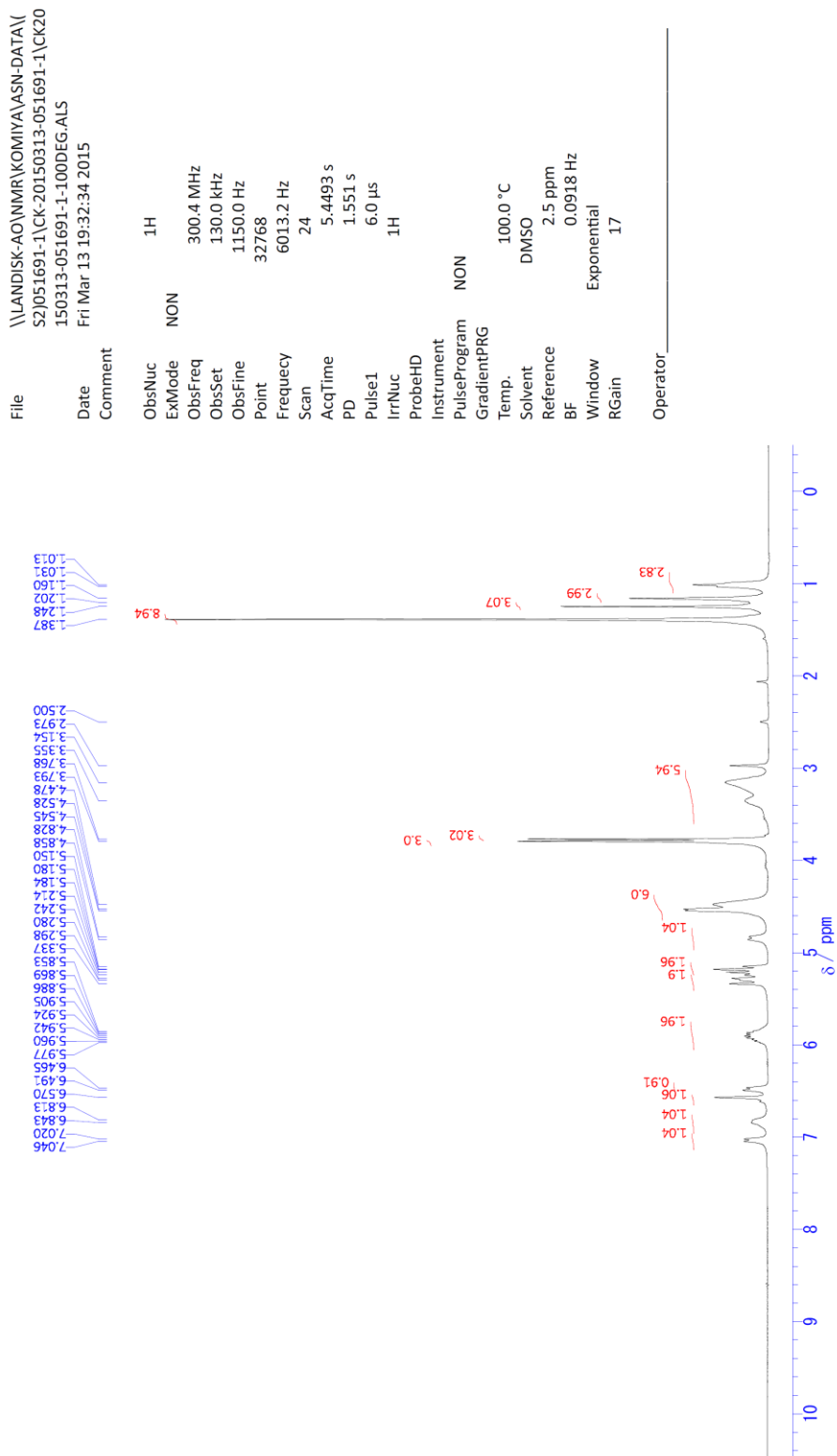
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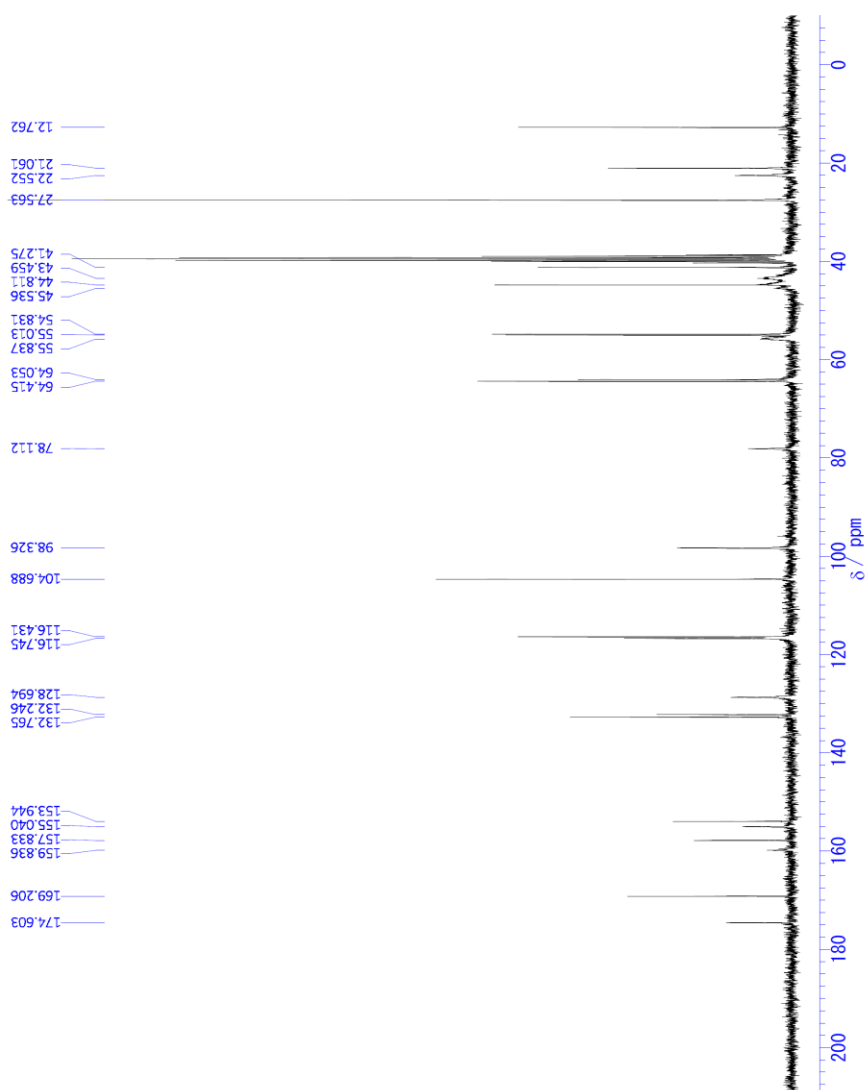


Allyl (S)-3-[(allyloxycarbonyl)amino]-4-{[2-ethyl(*tert*-butoxycarbonyl)aminoethyl][2,4-dimethoxybenzyl]amino}-2,2-dimethyl-4-oxobutanoate **26**

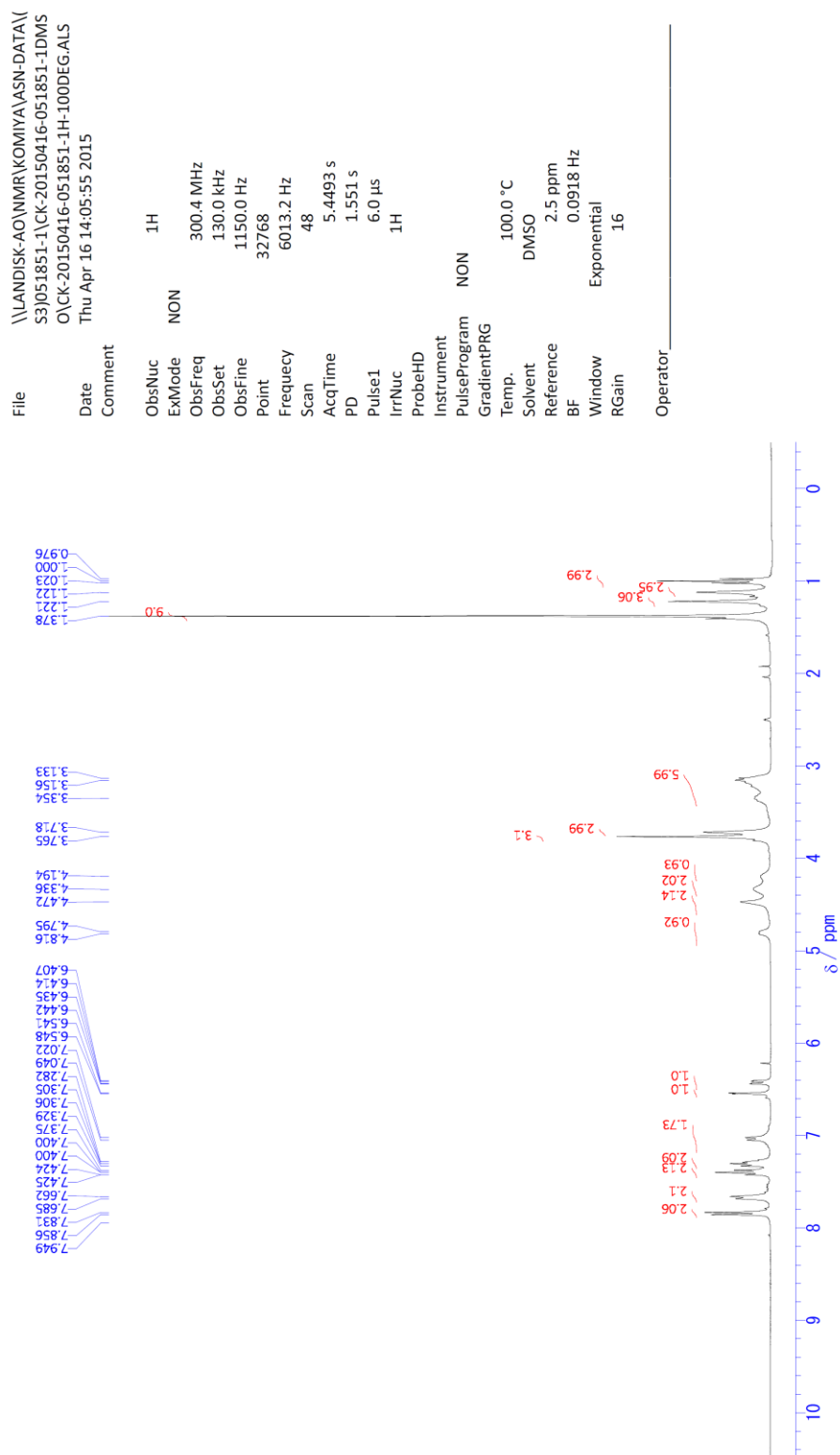


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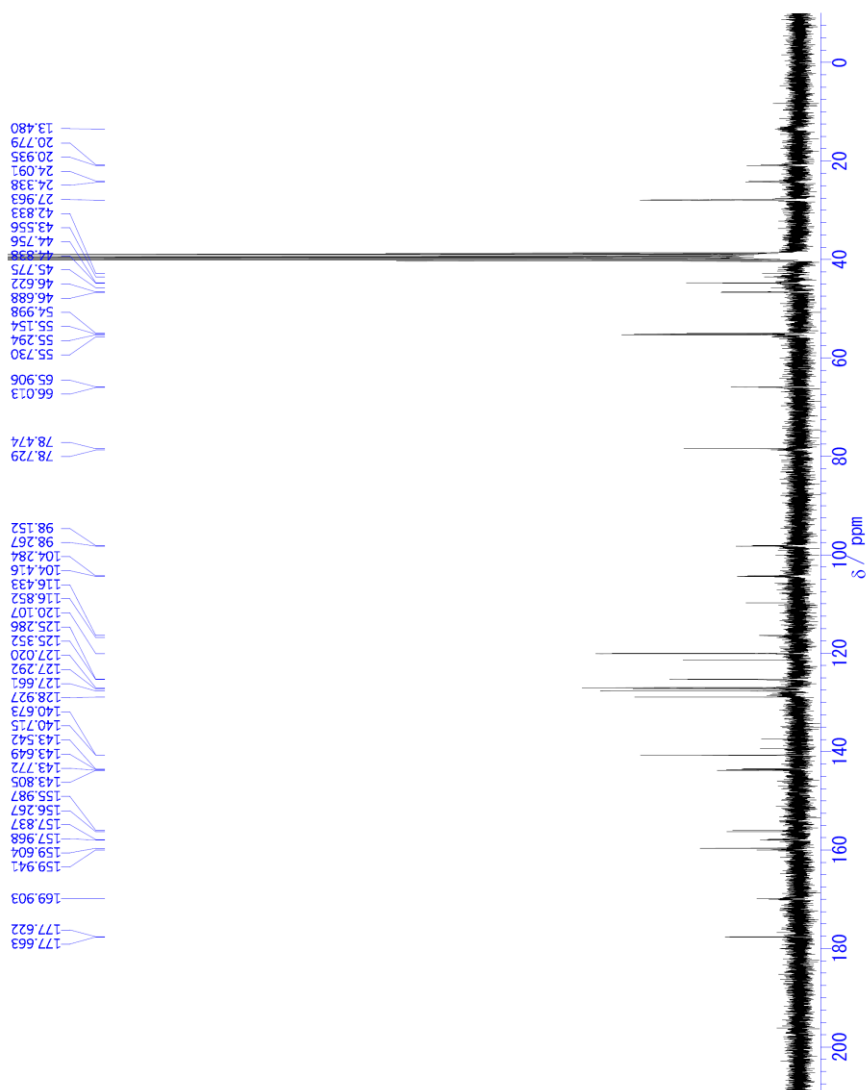


(S)-3-{-[(9H-Fluoren-9-yl)methoxycarbonyl]amino}-4-{[2-ethyl(*tert*-butoxycarbonyl)aminoethyl]  
[2,4-dimethoxybenzyl]amino}-2,2-dimethyl-4-oxobutanoic acid **27**

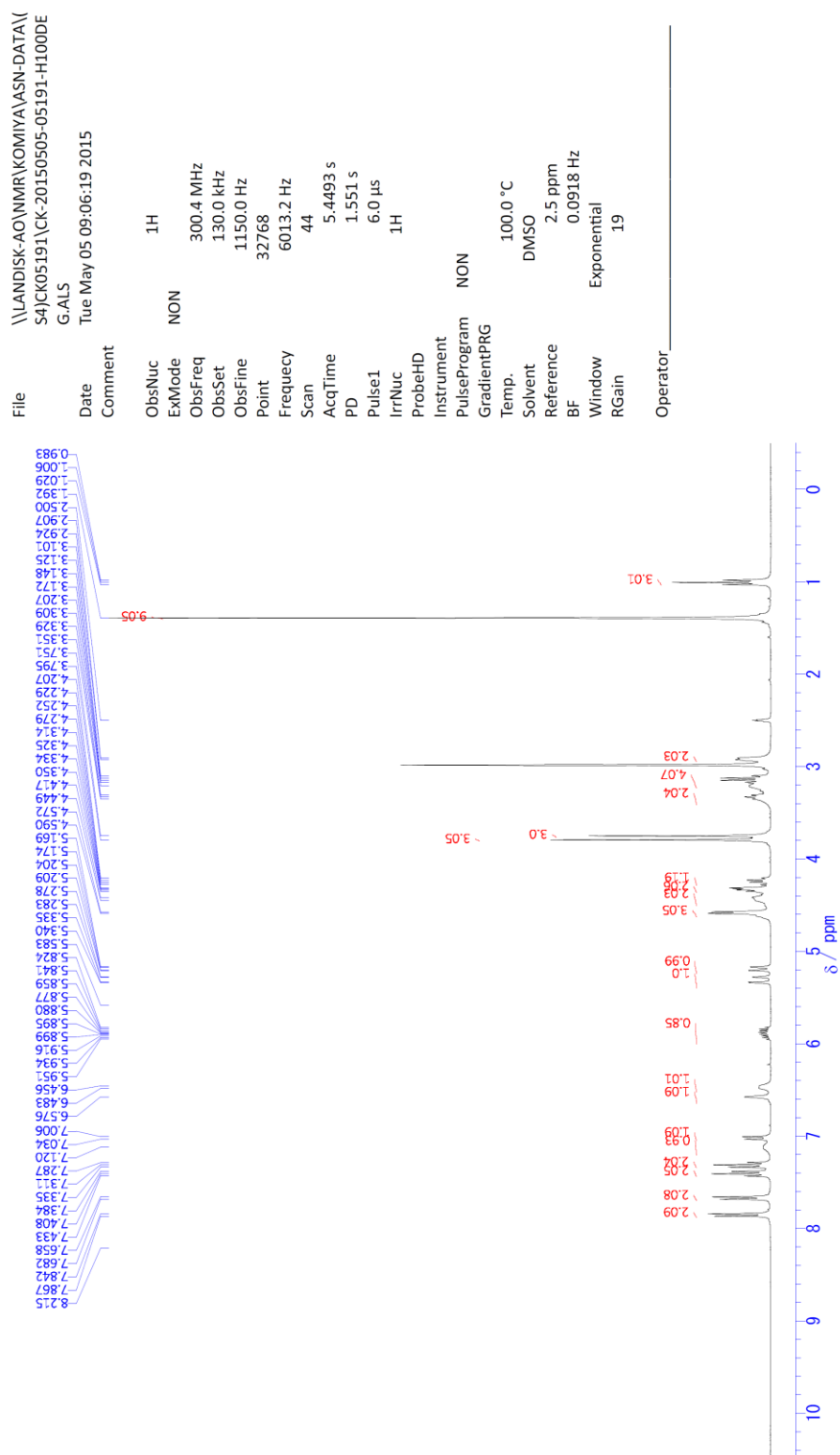


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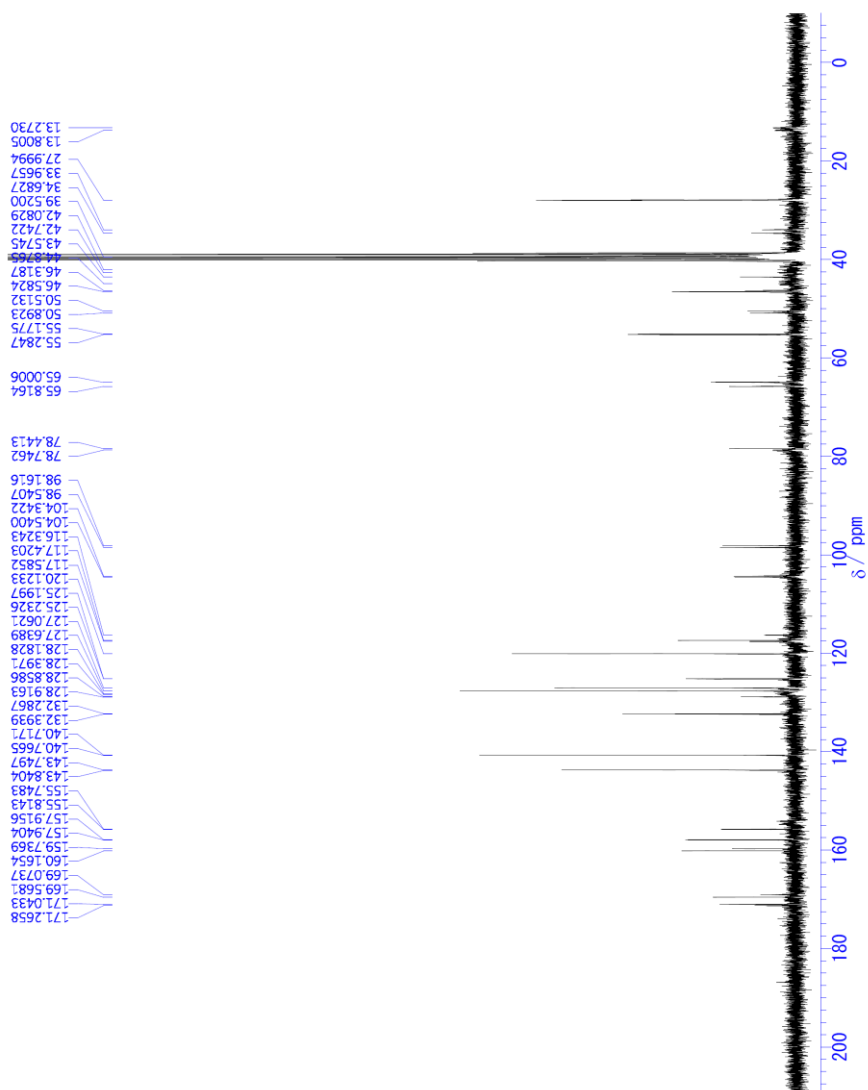


Allyl N<sup>2</sup>-{[(9H-Fluoren-9-yl)methoxy]carbonyl}-N<sup>4</sup>-{2-[(*tert*-butoxycarbonyl)(ethyl)amino]ethyl}-  
N<sup>4</sup>-(2,4-dimethoxybenzyl)-*L*-asparaginate **28**

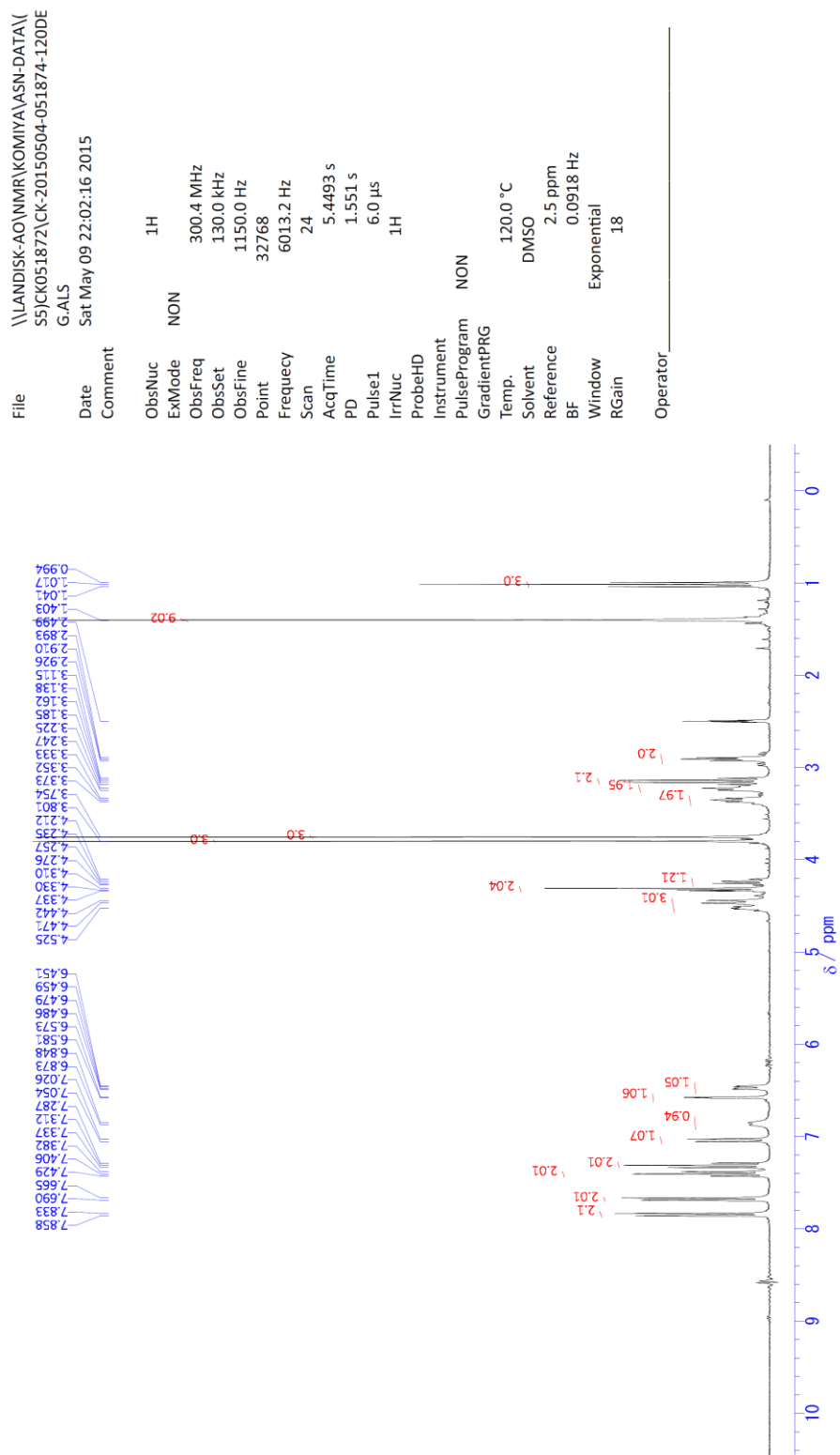


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Pulse1	5.0 $\mu$ s
IrrNuc	1H
ProbeHD	
Instrument	BCM
PulseProgram	
GradientPRG	
Temp.	25.0 $^{\circ}$ C
Solvent	DMSO
Reference	39.52 ppm
BF	0.3114 Hz
Window	Exponential
RGain	24
Operator	



N<sup>2</sup>-{[(9H-Fluoren-9-yl)methoxy]carbonyl}-N<sup>4</sup>-{2-[(*tert*-butoxycarbonyl)(ethyl)amino]ethyl}-N<sup>4</sup>-(2,4-dimethoxybenzyl)-*L*-asparagine **29**





File \\LANDISK-AO\NMR\KOMIYA\ASN-DATA\SS\CK051872\1C-NMR\CK-20150505-05187  
41-2BCM\_E1.ALS  
Date Tue May 12 08:10:30 2015  
Comment

ObsNuc	13C
ExMode	BCM
ObsFreq	75.45 MHz
ObsSet	124.0 kHz
ObsFine	1840.0 Hz
Point	32768
Frequency	20356.2 Hz
Scan	12000
AcqTime	1.6097 s
PD	0.9 s
Pulse1	5.0 $\mu$ s
IrrNuc	1H
ProbeHD	
Instrument	BCM
PulseProgram	
GradientPRG	
Temp.	25.0 $^{\circ}$ C
Solvent	DMSO
Reference	39.5 ppm
BF	0.3106 Hz
Window	Exponential
RGain	24
Operator	

